

Quantum Monte Carlo Vibrational Dynamics in a Property-Based Interaction Potential Scheme for Weakly Bound Clusters

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ABSTRACT

The typical shallowness of the potential surfaces of weakly bound clusters implies sizable ground-state vibrational excursions in the weak modes, a feature often complicated by considerable anharmonicity. The difficulties of vibrational analysis are exacerbated as the number of weak modes increases with the number of molecules in a cluster. Quantum Monte Carlo (QMC) approaches offer a general suitability to the problem of vibrational dynamics of weakly bound clusters in that they can fully account for anharmonicity and large amplitude motions. We report on the effectiveness and convergence behavior of diffusion quantum Monte Carlo for both energies and the key spectroscopic values of vibrationally averaged rotational constants. QMC involves recurring evaluations of the interaction potential, and we show how property-based, two- and three-body potentials (e.g., those involving intrinsic molecular tensor properties) may be carefully linked to the QMC propagation steps. © 1997 by John Wiley & Sons, Inc.

Introduction

A characteristic feature of weakly bound clusters, meaning those with well depths of less than about 40 kJ mol^{-1} per pair of molecules, is that the potential surfaces are shallow, often with extended troughs or other regions of flatness. These

surfaces tend to be quite anharmonic, and the shallowness of the potential wells means that even ground-state vibrational excursions can lead well away from the equilibrium. Because the vibrational dynamics tend to be complicated, an equilibrium structure is a poorer characterization of the on-average existence of a weakly bound cluster than it is for a chemically bound, small molecule. As experimental work continues to unfold for clusters beyond dimers (e.g., refs. 1–4), we have not

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only a greater complexity of cluster vibrations to analyze, but also an improving prospect of a solid link between gas and condensed phases. To fully understand the manifestations of weak bonding in dimer clusters and those just beyond dimers, it is essential to account for the effects of weak mode vibrations.

There are many approaches for studying vibrational dynamics. Recent interest in vibrational and vibrational-rotational analysis has grown, in part, because of the complexity inherent in floppy systems. Among contemporary developments is the discrete variable representation of Bacic and Light,⁵ which has been applied to the rotational-vibrational states of several weakly bound complexes (e.g., refs. 6, 7). There is also the collocation approach of Yang and Peet⁸⁻¹⁰ which is designed to handle strong coupling among vibrational degrees of freedom, the pseudospectral method of Friesner,¹¹ and diffusion quantum Monte Carlo (DQMC) which originates with Anderson's development¹² and has been employed and extended with attention to problems of weakly bound complexes by Watts et al.¹³ and Quack and Suhm.¹⁴ All but the QMC methods involve explicit or implicit bases and integration, sometimes as a quadrature, and/or they involve matrix diagonalization. With DQMC, the equivalent of integration of the Hamiltonian is accomplished by evaluation of the potential at numerous geometries and the search for the energy eigenvalue is accomplished via imaginary-time propagation. DQMC probably offers the greatest generality in application to different types and sizes of clusters, because it does not involve a basis set, a basis set equivalent, or integration. Its general use for excited states, however, is not always assured, and this might make it less competitive with respect to other methods when spectroscopic transition energies are sought.

One interest in DQMC arises from wishing to calculate on-average spectroscopic parameters and properties for weakly bound clusters in their ground states. In turn, DQMC can be used for part of the process of constructing interaction potentials¹⁵ in somewhat of a feedback loop. There are a considerable amount of microwave data (e.g., rotational constants) available for many weakly bound clusters. Often, the floppiness of these clusters is an obstacle in extracting a meaningful "structure" (equilibrium, on-average, or otherwise), one that could be used to assess the accuracy of an interaction potential. On the other hand, calculation of the direct experimental values, the rotational constants in the ground vibrational state, is a surer

assessment, and so repeated calculation with different potential parameters is a means of optimizing a potential. In this type of a cycle of calculations, the DQMC results determine refinements in the potential parameters. This makes the convergence behavior of DQMC, not only in the energy but also in the rotational constants, a more essential issue than in a single evaluation.

The process of diffusion quantum Monte Carlo comes about¹² from recognizing an equivalence of the differential equation for diffusion and the time-dependent differential Schrödinger equation. The Schrödinger equation is of the form of a diffusion equation if the time variable, t , is replaced by an imaginary time variable, τ ($\tau = it$). Monte Carlo (MC) techniques used to obtain a numerical solution of the diffusion equation can then be used to solve the modified Schrödinger equation. In solving a diffusion equation, particles are moved in randomized, discrete time steps and then may be replicated or destroyed depending on the energetic favorability of where a particle has been moved. An exact solution corresponds to the limiting case of an infinite number of diffusing particles, the length of the time steps approaching zero, and the number of time steps approaching infinity. In DQMC, pseudo-particles, "psips,"¹² propagate in imaginary time (τ). At a particular instant in imaginary time, each psip represents a particular geometrical arrangement of the atoms/molecules in the system. At that arrangement, the potential energy is evaluated and used to decide on replicating or destroying a psip. It is also used in finding the average energy of the collection of psips. After a "long" span of many time steps, the distribution of psips will reflect one state (the ground state, generally) because of the exponential decay in imaginary time of high energy states that may have been mixed initially. One may consider the long-time distribution of psips in geometrical space as the equivalent of a numerical representation of the wave function: A psip is a specific geometrical arrangement and the more favorable regions of space display the greater density of psips. So, just as for an MC solution of a diffusion equation, an exact result in DQMC is approached as the number of psips (instead of particles) and the number of time steps go to infinity with the size of the time steps going to zero.

Only the potential energy is evaluated in the DQMC propagation process. The kinetic energy operator in the Schrödinger equation plays its role in the randomized selection of the movement of the psips in a given time step.¹⁶ For this to be

possible, the kinetic energy must be separable in the geometrical degrees of freedom. The kinetic energy of a single point mass, $(p_x^2 + p_y^2 + p_z^2)/(2m)$, satisfies this requirement, and so DQMC is particularly straightforward for systems of point masses. Analyzing the vibrations of weakly bound clusters, however, does not necessarily call for relaxing the internal structures of the weakly attached species. The $3N$ degrees of freedom for a molecules composed of N point masses (atoms) are not all of concern. Constituent molecules in a cluster may be treated approximately as rigid species. This amounts to a quasi-Born–Oppenheimer separation of the relative fast intramolecular vibrations from the usually slower intermolecular (weak mode) vibrations. Eliminating high frequency motions should allow for the use of longer time steps for a given level of precision, and that translates into fewer steps for a simulation to span a fixed interval of time. Also, for other than small molecules, the rigidity assumption reduces the number of degrees of freedom and thereby the cost of a calculation.

Rigid molecule DQMC (or rigid body, RBDMC) calculations have been reported for weakly bound dimers.^{15,17–19} Recently, Gregory and Clary have developed a rigid body quantum Monte Carlo technique for directly obtaining tunneling splittings in clusters.²⁰ There has also been a very recent implementation of rigid body DQMC applied to the problem of a diatomic molecule surrounded by rare gas atoms.²¹ A detailed examination of the convergence of both the energy and the rotational constant remains to be done, and that is the objective of this report. Such information is essential for using DQMC in refining parameters in interaction potentials, which brings up another objective, integrating DQMC with a property-based cooperative (not strictly pairwise additive) potential.

Theoretical and Computational Approach

QMC propagation of rigid bodies (i.e., molecules) is different from propagation of point-mass particles. The propagation of rigid bodies is a combination of translational motion of their mass centers and rotation about their mass centers. For the Hamiltonian to have the necessary form to exploit the equivalence with a diffusion equation, the propagation of rotation about mass centers

needs to be done about each of the three principal axes (a, b, c) of the molecule so that the kinetic energy has the separable form, $(J_a^2/2I_a + J_b^2/2I_b + J_c^2/I_c)$ where I_a , I_b , and I_c are the principal moments of inertia. Special treatment can be done for linear molecules,²¹ because there are only two rotational degrees of freedom and because of the equivalence of the two moments of inertia. For a general analysis, we note that, with the moments of inertia taking the place of the masses, rotation may be treated on the same footing as translation.^{17,20} The calculational complication is in rotating molecules about their principal axes starting from an essentially arbitrary orientation of a given psip. An outline of how our procedure differs from the treatment of point masses, and how the potential evaluation is integrated with the diffusion steps, is as follows:

1. An initial geometry is selected for each molecule, i , in a cluster. This is a selection of the location of the molecule's mass center plus a selection of rotations about each of the three principal axes of the molecule. A matrix, \mathbf{U}_i , is calculated from these orientation angles of the i th molecule. This matrix is the transformation to the molecule's orientation from a reference orientation wherein its principal axes are aligned with the laboratory axes.
2. At each time step and for each psip, in addition to translating the mass centers of molecules by small increments ("diffusing"), the molecules are rotated about their principal axes by some small angular increments, designated $\{\delta R_a, \delta R_b, \delta R_c\}_i$ where the i subscript refers to the i th molecule. These rotation increments are Monte Carlo selected the same as translation increments.¹⁶
3. At each time step, for each psip and each molecule, the current \mathbf{U}_i is updated according to the rotations $\{\delta R_a, \delta R_b, \delta R_c\}_i$.
4. Each \mathbf{U}_i transformation matrix is applied to the permanent dipole and quadrupole moments of the i th molecule in its reference orientation to obtain the components of the molecule's moments at the current orientation. Then, the field and field gradient components that a given molecule experiences from nearby molecules are evaluated in the laboratory axis system by summation. The resulting total field and field gradient components experienced by a given molecule are

rotated back (\mathbf{U}^{-1}) so as to be expressed in the principal axis system of the given molecule whereupon its electrical interaction energy is directly evaluated. (Permanent moment-permanent moment interactions are scaled by 0.5 to remove overcounting.) This sequence of steps evaluates the polarization energies of each molecule without having to transform the polarizability tensors to the laboratory axis system.

A crucial computational element of the procedure is that of step 3, updating the \mathbf{U} matrices for some given small rotation about principal axes. This is accomplished via the construction of three matrices. For some unit vector $\vec{n} = (x, y, z)$, the unitary transformation matrix, \mathbf{W} , for a rotation about this vector by an angle, θ , is²²:

$$\mathbf{W} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \sin \theta \begin{pmatrix} 0 & -z & y \\ z & 0 & -x \\ -y & x & 0 \end{pmatrix} + 2 \sin^2(\theta/2) \begin{pmatrix} -y^2 - z^2 & xy & xz \\ xy & -x^2 - z^2 & yz \\ xz & yz & -x^2 - y^2 \end{pmatrix}$$

We let \vec{n} be the direction of the molecule's principal axis that is aligned with the laboratory x -axis in the reference orientation, and so the components of \vec{n} are the elements of the first row of the current \mathbf{U} matrix. Then, θ is the corresponding increment from the set $\{\delta R_a, \delta R_b, \delta R_c\}_i$. \mathbf{W} is constructed according to the formula, and then \mathbf{U} is multiplied by \mathbf{W} to yield the \mathbf{U} matrix updated for this first rotation about a principal axis. Next, the process is repeated with \vec{n} being the direction of the molecule's principal axis that is aligned with the laboratory y -axis in the reference orientation; that is, \vec{n} is the second row-vector in \mathbf{U} . \mathbf{U} is multiplied by the resulting \mathbf{W} from this rotation. And finally, a rotation is performed with \vec{n} being the direction of the molecule's principal axis that is aligned with the laboratory z -axis in the reference orientation. In this way, three successive small angle rotations about principal axes of a molecule, whatever its current orientation, are performed. On the basis of a separate implementation, we have found this process is equivalent in effect and in computational cost to the use of quaternions, a mathematical device for carrying out rotations about arbitrarily oriented vectors that has been used in classical molecular dynamics simulations.^{23,24}

The expression above for \mathbf{W} is valid only if \vec{n} is normalized, and the sequence of rotations about three axes requires that they be strictly orthogonal. After many successive diffusion steps, the limits on a computer's numerical precision can lead to deviations from orthonormality, and ultimately serious errors. ON the DEC AXP systems used for the calculations reported here, we have found very small deviations in final energies and rotational constants starting to be noticeable in as few as 2000 steps. This numerical problem, however, is easily overcome. Prior to forming a set of three \mathbf{W} matrices (for rotation about the three principal axes), the rows of a current \mathbf{U} matrix are simply Schmidt orthonormalized. As well, we have found that the Schmidt orthonormalization need not be done on every step. In a lengthy, 60,000-step dimer run, there were only small differences between doing this every step versus doing it every 3000 steps. The convergence tests reported here are based on assuring orthonormalization on every step. The default choice for future calculations done with our program is a very conservative one that insures high numerical precision, doing the Schmidt orthonormalization every tenth diffusion step.

Site-site (zero rank tensor) interaction potentials do not call for rotational transformations, and sometimes this makes them seem more favorable than potentials involving, say, a dipole moment (first rank tensor) and a dipole polarizability (second rank tensor). However, if the molecules are rigid, the generation of \mathbf{U}_i matrices for each psip is intrinsic to an efficient rotational propagation procedure, and the use of tensor properties in an interaction potential proceeds by simply applying the \mathbf{U} s as outlined above. In other words, limitation to pointwise potentials is unnecessary when assuming molecular rigidity and its consequent reduction in the number of degrees of freedom. A very direct integration of using a property-based potential evaluation with DQMC develops in this way, and we foresee this approach as useful for large molecule problems wherein functional groups, but not necessarily an entire molecule, are taken as the rigid constituents.

Results and Discussion

The water dimer was used for the examination of convergence behavior. The potential interaction scheme is based on, but somewhat different from,

the molecular mechanics for clusters (MMC) model.²⁵ This potential includes the electrical interaction energy developing via the molecular dipole, quadrupole, the dipole polarizability, the dipole–quadrupole polarizability, and the quadrupole polarizability. There is direct polarization, but no back or mutual polarization, and so there are pairwise contributions plus three-body (three-molecule) cooperative terms. There is a non-electrical part of the potential, as in MMC, which is an atom–atom “6–12” potential. For a pair of molecules, *A* and *B*, it has the following form:

$$V_{AB}^{(\text{non-el.})} = \sum_i^{A \text{ atoms}} \sum_j^{B \text{ atoms}} \left(\frac{d_{A_i} d_{B_j}}{|\vec{r}_{A_i} - \vec{r}_{B_j}|^2} - \frac{c_{A_i} c_{B_j}}{|\vec{r}_{A_i} - \vec{r}_{B_j}|^6} \right)$$

The parameters (in a.u.) that were used in studying the convergence behavior are: *c*_H = 0.6; *d*_H = 6.6, *c*_O = 7.8; and *d*_O = 1740. These are parameters that we have previously used for water¹⁵; however, with the convergence information we report here, refinements in these parameters have been obtained as well.

There are three specifications in a DQMC calculation that control the computation time and affect the accuracy of the result. The first is the number of psips, *N*_ψ, something we may loosely associate with the fineness/number of points of an irregular grid in a numerical representation of a wave function. The second specification is the length of the (imaginary) time steps in the propagation, *τ*. The third is the number of time steps, *N*_τ. The total time for propagation is *τN*_τ. Calculations were carried out for the water dimer with 142 selections

TABLE I. Energy Convergence for (H₂O)₂: Standard Deviation (cm^{−1}).

| Number of time steps | Number of psips | Length of time steps (a.u.) | | | | |
|----------------------|-----------------|-----------------------------|------|------|------|------|
| | | 12 | 25 | 50 | 100 | 200 |
| 1000 | 4000 | 1.74 | 2.12 | 1.70 | 1.47 | 0.94 |
| | 2000 | 5.58 | 4.02 | 1.79 | 1.51 | 1.90 |
| | 1000 | 7.19 | 4.39 | 4.41 | 1.96 | 1.78 |
| | 500 | 8.70 | 9.51 | 6.24 | 3.63 | 1.74 |
| 2000 | 4000 | 2.23 | 1.78 | 0.68 | 1.05 | 0.66 |
| | 2000 | 4.23 | 2.62 | 1.64 | 0.91 | 1.30 |
| | 1000 | 4.61 | 2.45 | 1.60 | 1.32 | 0.99 |
| | 500 | 4.45 | 6.65 | 4.57 | 2.32 | 1.23 |
| 4000 | 4000 | 2.58 | 1.15 | 0.28 | 0.78 | 0.35 |
| | 2000 | 2.73 | 1.51 | 0.60 | 0.85 | 0.60 |
| | 1000 | 3.31 | 1.40 | 1.21 | 1.14 | 0.74 |
| | 500 | 5.06 | 3.28 | 2.67 | 1.96 | 1.32 |
| 8000 | 4000 | 1.61 | 0.81 | 0.52 | 0.52 | 0.17 |
| | 2000 | 0.96 | 1.16 | 1.13 | 0.52 | 0.23 |
| | 1000 | 2.84 | 1.35 | 1.51 | 1.04 | 0.82 |
| | 500 | 4.59 | 2.38 | 2.07 | 0.51 | 1.20 |
| 16,000 | 4000 | 1.12 | 0.69 | 0.23 | 0.29 | 0.13 |
| | 2000 | 0.93 | 1.15 | 0.45 | 0.54 | 0.16 |
| | 1000 | 2.65 | 0.84 | 0.83 | 0.57 | 0.51 |
| | 500 | 4.08 | 1.94 | 1.44 | 0.59 | 0.68 |
| 32,000 | 4000 | 0.63 | 0.37 | 0.25 | 0.19 | 0.15 |
| | 2000 | 0.91 | 0.53 | 0.47 | 0.30 | 0.17 |
| | 1000 | 1.58 | 0.88 | 0.42 | 0.44 | 0.39 |
| | 500 | 1.88 | 1.37 | 1.04 | 0.56 | 0.45 |
| 64,000 | 4000 | 0.65 | 0.30 | 0.19 | 0.19 | 0.13 |
| | 2000 | 0.39 | 0.33 | 0.27 | 0.17 | 0.38 |
| | 1000 | 0.80 | 0.70 | 0.34 | 0.22 | 0.18 |
| | 500 | 1.50 | 0.74 | 0.73 | 0.34 | 0.36 |
| 128,000 | 2000 | | | 0.23 | | |
| | 1000 | | | 0.18 | | |
| | 500 | | | 0.51 | | |

of N_ψ , N_τ , and τ . Energies and rotational constants were obtained in each case, and their behavior helps to establish convergence with respect to the three control parameters. In addition to that information, ranges and standard deviations were obtained by partitioning each of the 142 calculations into 10 equal-sized parts and evaluating the energy and rotational constant for each part. The standard deviation is the rms deviation²⁶ of 10 values from the average of the 10 values. Tables I–IV give results for each of the 142 calculations, including the standard deviation in the energy (Table I), the total energy value (Table II), the range in the rotational constant (Table III), and the value of the rotational constant (Table IV).

The first conclusion from the results in Tables I–IV is that at $\tau = 12$, 25, and 50, the lengthiest

runs (biggest N_ψ and N_τ) appear to approach essentially the same energy and rotational constant values. However, $\tau = 100$ and 200 runs yield energies and rotational constants about 0.3% greater. Although this is small, it shows that, as τ becomes greater than 50 a.u., values are beginning to deviate from the value approached in the limit of a zero time step. A few spot tests were done setting $\tau = 400$, and then the differences with the short time step values were still more sizable. Thus, for weak vibrational modes, the highest precision in both energy and rotational constants calls for time steps up to about 50 a.u.

The next conclusion from the dimer results is that using 500 psips leads to differences of about 0.3% in the energy from using 4000 psips and differences of about 0.05% for rotational constants.

TABLE II.
Energy Convergence for (H₂O)₂: Average Energies^a (cm^{−1}).

| Number of time steps | Number of psips | Length of time steps (a.u.) | | | | |
|----------------------|-----------------|-----------------------------|-------|-------|-------|-------|
| | | 12 | 25 | 50 | 100 | 200 |
| 1000 | 4000 | 95.31 | 91.98 | 92.68 | 93.54 | 95.54 |
| | 2000 | 91.97 | 91.01 | 94.10 | 93.04 | 95.04 |
| | 1000 | 86.08 | 90.12 | 91.23 | 92.26 | 94.08 |
| | 500 | 93.45 | 93.88 | 86.57 | 92.70 | 92.07 |
| 2000 | 4000 | 95.05 | 92.07 | 92.93 | 93.53 | 95.69 |
| | 2000 | 92.59 | 92.70 | 93.09 | 93.07 | 95.48 |
| | 1000 | 86.65 | 90.13 | 91.15 | 92.58 | 94.66 |
| | 500 | 93.76 | 90.32 | 87.96 | 91.54 | 92.57 |
| 4000 | 4000 | 93.93 | 92.59 | 92.87 | 93.79 | 95.68 |
| | 2000 | 92.56 | 92.51 | 93.26 | 93.03 | 95.35 |
| | 1000 | 89.16 | 90.92 | 91.67 | 93.00 | 94.59 |
| | 500 | 93.99 | 91.78 | 88.28 | 91.02 | 93.34 |
| 8000 | 4000 | 93.18 | 92.63 | 93.01 | 93.66 | 95.69 |
| | 2000 | 92.54 | 92.44 | 93.13 | 93.09 | 95.33 |
| | 1000 | 90.54 | 90.99 | 91.80 | 92.37 | 94.40 |
| | 500 | 90.76 | 90.99 | 89.30 | 91.24 | 92.92 |
| 16,000 | 4000 | 93.14 | 92.71 | 92.99 | 93.61 | 95.74 |
| | 2000 | 92.38 | 92.79 | 92.97 | 93.25 | 95.27 |
| | 1000 | 91.46 | 91.48 | 91.68 | 92.31 | 94.33 |
| | 500 | 90.12 | 90.34 | 89.99 | 91.04 | 92.88 |
| 32,000 | 4000 | 92.95 | 92.85 | 93.07 | 93.61 | 95.73 |
| | 2000 | 92.58 | 92.56 | 92.69 | 93.27 | 95.34 |
| | 1000 | 92.15 | 91.65 | 91.70 | 92.44 | 94.51 |
| | 500 | 89.79 | 90.56 | 90.35 | 90.91 | 93.08 |
| 64,000 | 4000 | 92.83 | 92.98 | 93.16 | 93.62 | 95.65 |
| | 2000 | 92.58 | 92.55 | 92.77 | 93.32 | 95.32 |
| | 1000 | 91.83 | 91.85 | 91.99 | 92.53 | 94.40 |
| | 500 | 89.25 | 90.34 | 90.41 | 90.87 | 92.92 |
| 128,000 | 2000 | | | 92.68 | | |
| | 1000 | | | 91.89 | | |
| | 500 | | | 90.29 | | |

^a The total stability is -1100 cm^{-1} less the value listed. The results indicate a stability of $-1192.8 \pm 0.5 \text{ cm}^{-1}$.

TABLE III.
Property Convergence: Range in (H₂O)₂ Rotational Constant (MHz).

| Number of time steps | Number of psips | Length of time steps (a.u.) | | | | |
|----------------------|-----------------|-----------------------------|------|------|------|------|
| | | 12 | 25 | 50 | 100 | 200 |
| 1000 | 4000 | 32.4 | 21.4 | 11.9 | 13.1 | 11.2 |
| | 2000 | 32.7 | 25.8 | 15.5 | 33.1 | 14.7 |
| | 1000 | 94.6 | 51.4 | 27.9 | 21.3 | 12.3 |
| | 500 | 99.8 | 49.6 | 41.5 | 40.4 | 20.7 |
| 2000 | 4000 | 16.3 | 19.0 | 7.2 | 9.7 | 8.2 |
| | 2000 | 20.4 | 22.4 | 16.5 | 13.7 | 11.0 |
| | 1000 | 41.8 | 23.5 | 30.6 | 9.5 | 11.9 |
| | 500 | 44.2 | 43.3 | 30.1 | 12.7 | 14.1 |
| 4000 | 4000 | 9.1 | 9.6 | 7.0 | 4.2 | 4.4 |
| | 2000 | 27.0 | 16.9 | 10.7 | 8.4 | 8.0 |
| | 1000 | 32.0 | 9.4 | 16.9 | 8.7 | 7.4 |
| | 500 | 43.1 | 30.5 | 14.8 | 8.3 | 7.7 |
| 8000 | 4000 | 5.0 | 6.0 | 4.0 | 3.0 | 3.7 |
| | 2000 | 14.2 | 14.6 | 9.0 | 4.7 | 5.1 |
| | 1000 | 35.8 | 15.4 | 9.9 | 3.7 | 4.3 |
| | 500 | 30.5 | 30.8 | 15.6 | 9.2 | 8.8 |
| 16,000 | 4000 | 7.5 | 5.3 | 3.7 | 3.7 | 1.8 |
| | 2000 | 12.6 | 4.2 | 5.7 | 3.9 | 3.6 |
| | 1000 | 20.2 | 9.2 | 9.0 | 2.9 | 2.7 |
| | 500 | 18.6 | 7.2 | 13.4 | 6.5 | 4.6 |
| 32,000 | 4000 | 5.1 | 4.0 | 1.1 | 1.2 | 1.7 |
| | 2000 | 5.3 | 4.2 | 4.5 | 2.6 | 1.3 |
| | 1000 | 11.1 | 6.5 | 5.4 | 5.1 | 1.6 |
| | 500 | 10.1 | 8.5 | 13.3 | 4.7 | 4.4 |
| 64,000 | 4000 | 4.1 | 1.5 | 3.2 | 1.5 | 1.3 |
| | 2000 | 6.2 | 5.1 | 2.7 | 1.8 | 1.3 |
| | 1000 | 7.8 | 4.4 | 3.1 | 2.5 | 2.2 |
| | 500 | 8.4 | 9.3 | 5.6 | 4.2 | 2.9 |
| 128,000 | 2000 | | | 1.2 | | |
| | 1000 | | | 1.7 | | |
| | 500 | | | 3.6 | | |

In contrast, 1000-psip results are within 0.1% and 0.2% of the 4000-psip energies and rotational constants, respectively. With this convergence with respect to the number of psips, the use of 1000–2000 psips should provide very high precision in both energy and vibrationally averaged properties. Of course, this number will depend somewhat on the number of vibrational degrees of freedom, and so with clusters of more than two molecules, the number of psips to achieve the same level of accuracy will be greater.

A third conclusion is that standard deviations and ranges of values for both rotational constants and energies depend on the product τN_r , which is the length of (imaginary) time of the propagation. If this is equal to about 200,000 a.u., the standard deviation in the energy is mostly less than 1 cm⁻¹

and the standard deviation in the rotational constant is around 2 MHz. The most extensive calculation yields an energy of 1192.7 ± 0.2 cm⁻¹ and a rotational constant of 6108.5 ± 0.4 MHz. This rotational constant is less than the spectroscopic value of $\langle B + C \rangle / 2$ for the water dimer of 6161 MHz.²⁷ We have previously reported DQMC calculations on the water dimer¹⁵ with a different implementation that invoked certain assumptions that presumed small time steps and that was applied with less complete convergence information to select the control parameters. In that study, an energy of 1289 cm⁻¹ and a rotational constant of 6136 MHz were obtained with the same potential although not the same τ , etc., as used here.

The convergence behavior for the rotational constant is quite important in using spectroscopic

data for construction of interaction potentials, which in the case of our implementation means the selection of the c and d parameters. A map of the $\langle B + C \rangle / 2$ "surface" with respect to the four c and d "variables" would reveal the regions in the parameter space for which DQMC values most closely match the experimental value for $\langle B + C \rangle / 2$ of 6161 MHz.²⁷ However, a map may require more calculational effort than is necessary to optimally select the parameters. If a tolerance of say ± 20 MHz in the rotational constant were chosen, then parameter space may be scanned with relatively short calculations (small numbers of psips and small numbers of time steps). Regions that are within twice this tolerance of the target value (6161 MHz) can then be searched with a

stricter tolerance, such as ± 5 MHz, with lengthier calculations, but in a smaller region of parameter space. This rather obvious process of doing finer level searches while reducing the rms deviation in the QMC calculations may be easily carried to a 1-MHz agreement with the target value.

For the water dimer, successive reduction in rms error and optimization of c and d potential parameters rapidly yielded a rotational constant, $\langle B + C \rangle / 2$, within 1 MHz of the experimental value. It was found that a small, narrow trough exists in parameter space such that varying the repulsiveness of the hydrogens (the d_H parameter) along with the attractiveness of oxygen (the c_O parameter), maintains the rotational constant within 1 MHz of the target value of 6161 MHz.

TABLE IV.
Rotational Constant Convergence for $(H_2O)_2$: $\langle B + C \rangle / 2$ (MHz).

| Number of time steps | Number of psips | Length of time steps (a.u.) | | | | |
|----------------------|-----------------|-----------------------------|--------|--------|--------|--------|
| | | 12 | 25 | 50 | 100 | 200 |
| 1000 | 4000 | 6107.4 | 6105.0 | 6110.6 | 6115.1 | 6126.4 |
| | 2000 | 6104.4 | 6110.9 | 6107.4 | 6111.5 | 6129.1 |
| | 1000 | 6098.6 | 6106.7 | 6101.5 | 6112.3 | 6127.3 |
| | 500 | 6107.5 | 6100.9 | 6100.5 | 6109.2 | 6121.7 |
| 2000 | 4000 | 6107.3 | 6105.9 | 6109.6 | 6113.0 | 6126.4 |
| | 2000 | 6105.7 | 6110.7 | 6108.4 | 6112.4 | 6127.2 |
| | 1000 | 6097.2 | 6105.5 | 6103.4 | 6112.3 | 6126.4 |
| | 500 | 6108.2 | 6101.4 | 6101.5 | 6110.1 | 6123.3 |
| 4000 | 4000 | 6105.8 | 6105.5 | 6108.2 | 6113.7 | 6127.3 |
| | 2000 | 6104.1 | 6107.1 | 6107.3 | 6112.5 | 6126.8 |
| | 1000 | 6103.4 | 6107.7 | 6106.0 | 6111.9 | 6127.5 |
| | 500 | 6114.4 | 6106.6 | 6100.8 | 6112.3 | 6124.2 |
| 8000 | 4000 | 6105.1 | 6106.0 | 6109.4 | 6113.6 | 6127.6 |
| | 2000 | 6106.9 | 6107.4 | 6108.1 | 6112.6 | 6126.9 |
| | 1000 | 6102.5 | 6105.7 | 6106.4 | 6112.1 | 6126.4 |
| | 500 | 6112.7 | 6103.2 | 6104.1 | 6111.9 | 6123.1 |
| 16,000 | 4000 | 6105.5 | 6106.5 | 6109.2 | 6113.7 | 6127.9 |
| | 2000 | 6106.3 | 6107.0 | 6108.0 | 6113.4 | 6126.5 |
| | 1000 | 6106.6 | 6104.7 | 6108.1 | 6112.3 | 6126.4 |
| | 500 | 6106.6 | 6103.4 | 6106.0 | 6110.9 | 6123.7 |
| 32,000 | 4000 | 6106.1 | 6107.1 | 6109.2 | 6113.7 | 6128.2 |
| | 2000 | 6106.1 | 6106.9 | 6108.9 | 6113.6 | 6126.9 |
| | 1000 | 6106.4 | 6104.9 | 6107.4 | 6112.4 | 6126.4 |
| | 500 | 6107.6 | 6103.9 | 6105.7 | 6110.8 | 6124.4 |
| 64,000 | 4000 | 6106.3 | 6107.5 | 6109.3 | 6113.9 | 6127.8 |
| | 2000 | 6106.0 | 6106.7 | 6108.5 | 6113.7 | 6127.0 |
| | 1000 | 6105.8 | 6105.5 | 6108.1 | 6112.8 | 6126.3 |
| | 500 | 5107.1 | 6105.2 | 6105.7 | 6111.0 | 6124.2 |
| 128,000 | 2000 | | | 6108.5 | | |
| | 1000 | | | 6108.1 | | |
| | 500 | | | 6106.4 | | |

This simply illustrates that four parameters are not uniquely determined by one rotational constant; however, the narrowness of this region of parameter space does not support the prospect of widely different parameter choices leading to agreement with the observed rotational constant value.

Within the parameter space trough where $\langle B + C \rangle / 2$ is 6161 ± 1 MHz for $(\text{H}_2\text{O})_2$, a search was made for the rotational constant of $(\text{D}_2\text{O})_2$ for which the experimental value is 5432 MHz.²⁷ This was done by simply using the deuterium mass in place of the mass of hydrogen, and otherwise carrying out the same calculation. Of course, the on-average O—D bond in D_2O is 0.004 Å shorter than the on-average O—H bond in H_2O ,²⁸ and this can affect the interaction potential and the rotational constant. The slightly shorter on-average bond implies slightly different on-average electrical properties for the two isotopic forms, and that may slightly influence the potential. The difference in structures may also mean there are slight differences in the dispersion and exchange repulsion interactions, features represented in the model potential via the c and d parameter terms. In other words, the type of potential we have should have parameters and properties specific to D_2O . Short of that, we may simply evaluate the most direct effect of contracting the on-average O—H/D bond by evaluating the equilibrium rotational constant for $(\text{D}_2\text{O})_2$ using the equilibrium structure of $(\text{H}_2\text{O})_2$ as obtained from the model potential, first with the bond length used for H_2O and then with a bond length 0.004 Å shorter. The latter yields a rotational constant 7 MHz greater than the former, and so simply using the mass of D in place of the mass of H introduces an approximately 7-MHz overshoot in the DQMC results for $(\text{D}_2\text{O})_2$.

Our search through parameter space trough wherein the rotational constant of $(\text{H}_2\text{O})_2$ is 6161 MHz yielded a rotational constant for $(\text{D}_2\text{O})_2$ of 5480 MHz, which is 48 MHz greater than the spectroscopic value, about 7 MHz of which we attribute to the overshoot from not correcting for on-average differences in bond length between isotopic forms. The parameter values (in a.u.) that gave this result were: $c_{\text{H}} = 0.6$; $d_{\text{H}} = 8.9$; $c_{\text{O}} = 7.95$; and $d_{\text{O}} = 1665$. So, with the demonstrated convergence behavior in rotational constants, and with a varying convergence limit for searching parameter space, an interaction potential for rigid water molecules integrated with DQMC has been optimized.

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